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Webster

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(54) **POLYOLEFIN ARTICLES WITH LONG-TERM ELEVATED TEMPERATURE STABILITY**

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(57) **ABSTRACT**

What is disclosed are polyolefin compounds, e.g., polyethylene and polypropylene, and articles therefrom made in by conventional solid, melt-phase compounding with oxidized, non-cationized, non-silylated sulfur black pigment, a phenolic antioxidant and a sulfur-containing secondary stabilizer, each in stabilizing amount, specified below, which provide a synergistic improvement in the long term heat aging of polyolefins. Preferably the sulfur black compound is treated by washing, and reduction in the soluble sodium salts.

Also disclosed is melt-phase compounded polyolefin and molded articles made therefrom comprising incorporating of carbon black, oxidized, non-cationized, non-silylated sulfur black pigment, a phenolic antioxidant and sulfur-containing secondary stabilizer.

21 Claims, 6 Drawing Sheets

2,2'-oxalyidiamidobisethyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (NAUGARD XL 1);

2,2'-methylenebis(4-ethyl-6-tert-butylphenol) (CYANOX 425);

2,2'-methylenebis[6-(1-methylcyclocyclohexyl)-p-cresol];

4,4'-thiobis(6-t-butyl-o-cresol);

2,2'-thiobis[4,6-di-tert-butyl-m-cresol] (TOPANOL® TP);

2,2'-thiobis[4,6-di-tert-butyl-o-cresol] (SANTANOX® R);

4,4'-thiobis (3-methyl-6-t-butyl phenol) (IRGANOX 415) (SEENOX® BCS);

thiobisdiethylenebis(3,5-di-t-butyl-4-hydroxy) hydrocinnamate (IRGANOX 1035);

butyric acid, 3,3-bis(3-t-butyl-4-hydroxyphenyl) ethylene ester;

2,2'-ethylidenebis(4,6-di-t-butylphenol);

2,2'-thiobis(4-methyl-6-tert-butylphenol) (IRGANOX 1081);

bis[4-(2-phenyl-2-propyl)phenyl] amine (NAUGARD 445);

N,N-dimethyl(3,5-di-tert-butyl-4-hydroxybenzyl) amine (ETHANOX 703);

4,4'-di-tert-octyidiphenylamine (VANOX 1081);

1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane (NONOX® WSO); and

1,6-hexamethylene bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (IRGANOX L09);

the polyphenols, like 1,3,5-tris(4-t-butyl-3-hydroxyl-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H, 3H, 5H)-trione;

tetrakis[methylene(3,5-di-t-butyl-4-hydroxy) hydrocinnamate]methane;

1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-s-triazine-2, 4,6-(1H, 3H, 5H)-trione (GOOD-RITE 3114);

1,3,5-tris(2,6-dimethyl-3-hydroxy-4-tert-butylbenzyl) isocyanurate (CYANOX® 1790);

trimethyl-2,4,6-tris(3,5, -di-t-butyl-4-hydroxybenzyi) benzene);

tris(3,5, -di-t-butyl-4-hydroxybenzyl)isocyanurate;

tris(3,5-di-tert-butyl-4-hydroxyphenyl)phosphate (ETHANOX ® 796);

hydrocinnamic acid, 3,5-di-t-butyl-4-hydroxy-, triester with 1,3,5-tris(2-hydroxyethyl)-s-triazine-2,4,6-(1H, 3H, 5H)-trione (GOOD-RITE® 3125);

1,1,3-tris((2-methyl-4-hydroxy-5-t-butylphenyl)butane) (TOPANOL CA);

3,5-bis((3,5-di-tert-butyl-4-hydroxy)benzyl)-2,4,6-trimethylphenol (IRGANOX® 1299);

and pentaerythritol tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (IRGANOX 1010);

and other suitable antioxidants, including calcium bis (ethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate) (IRGANOX 1425);

o,o-dimethyl o-(4-cyanophenyl) phosphorothioate (SUMITOMO S 4084);

terephthalic acid, 1,4-dithio-,S,S-bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenztl)ester (CYANOX 1729);

triethylene glycol bis(3-tert-butyl-4-hydroxy-5-methylhydrocinnamate)(AO 70);

hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate (IRGANOX 259);

1,2-bis(3,5, -di-tert-butyl-4-hydroxyhydrocinnamoyl) hydrazide (IRGANOX 1024);

4,4'-di-tert-octyldiphenamine (NAUGALUBE® 438R);

phosphonic acid, (3,5-di-tert-butyl-4-hydroxybenzyl)-, dioctadecyl ester (IRGANOX 1093);

1,3,5-trimethyl-2,4,6-tris(3',5'-di-tert-butyl-4'hydroxybenzyl)benzene (IRGANOX 1330); 2,4-bis (octylthio)-6-(4-hydroxy-3,5-di-tert-butylanilino)-1,3, 5-triazine (IRGANOX 565); isooctyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (IRGANOX 1135);

octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (IRGANOX 1076);

3,7-bis(1,1,3,3-tetramethylbutyl)-10H-phenothiazine (IRGANOX LO 3);

2,2'-methylenebis(4-methyl-6-tert-butylphenol) monoacrylate (IRGANOX 3052);

2-tert-butyl-6-[1-(3-tert-butyl-2-hydroxy-5-methylphenyl)ethyl]4-methylphenyl acrylate (SUMILIZER TM 4039);

2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]4,6-di-tert-pentylphenyl acrylate (SUMILIZER GS);

1,3-dihydro-2H-Benzimidazole (SUMILIZER® MB);

2-methyl-4,6-bis[(octylthio)methyl]phenol (IRGANOX 1520);

N,N'-trimethylenebis-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionamide (IRGANOX 1019);

4-n-octadecyloxy-2,6-diphenylphenol (IRGANOX 1063);

2,2'-ethylidenebis[4,6-di-tert-butylphenol] (IRGANOX 129);

N,N'-hexamethylenebis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide) (IRGANOX 1098);

diethyl(3,5-di-tert-butyl-4-hydroxybenxyl)phosphonate (IRGANOX 1222);

4-octyl-N-(4-octylphenyl)-benzenamine (ANOX NS);

4,4'-di-tert-octyidiphenylamine(IRGANOX 5057);

N-phenyl-1-napthalenamine IRGANOX L 05);

2,2,4-trimethyl-1,2-dihydroquinoline polymer (ANOX® HB);

tris[2-tert-butyl-4-(3-ter-butyl-4-hydroxy-6-methylphenylthio)-5-methyl phenyl] phosphite (HOSTANOX OSP 1);

zinc dinonyidithiocarbamate (HOSTANOX VP-ZNCS 1); and

3,9-bis[1,1-diimethyl-2-[(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy]ethyl]-2,4,8,10-tetraoxaspiro[5.5]undecane (SUMILIZER® AG80).

The preferred antioxidants are pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, sold as HOSTANOX® O 10; 1,3,4-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-s-triazine-2,4-(1H, 3H, 5H)-trione, or a mixture, and most preferred is 1,3,5-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-s-triazine-2,4-(1H, 3H, 5H)-trione.

The sulfur containing secondary antioxidant (C) are referred to as β-thioesters (—S—C—C—C(O)—OR) and